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^{13}C NMR SPECTROSCOPY OF 4,4"-METHYLENEBIS-(PHENYLISOCYANATE)/1,4-BUTANEDIOL/POLY(TETRAMETHYLENE ETHER GLYCOL) POLY(ETHER)URETHANES

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^{13}C NMR Spectroscopy of 4,4'-Methylenebis-(phenylisocyanate)/1,4-Butanediol/Poly(tetramethylene ether glycol) Poly(ether)urethanes

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Abstract

The solution and solid state ^{13}C NMR spectra of six 4,4'-methylenebis-(phenylisocyanate)/1,4-butanediol/poly(tetramethylene ether glycol) based poly(ether)urethane thermoplastic elastomers (TPEs) are presented. The spectra confirm that all six TPEs were synthesized from the same diisocyanate/diol/polyether glycol starting materials. Changes in the relative proportions of the starting materials were reflected in the intensity of carbon resonances associated with the urethane rich (diisocyanate rich) and polyether glycol rich portions of the polymer. Changes in the ratio of the intensities of carbons were found to correlate with the Shore D hardness of the polymers. A Goldman-Shen experiment was conducted on three of the TPEs. The results suggest that the Elastollan 1164D sample had larger interdomain spacing and therefore a greater degree of phase separation than the Texin 970D and Texin 950D samples.

Résumé

On présente les spectres RMN ^{13}C de six élastomères thermoplastiques de poly(éther)uréthanes (TPE), à base de 4,4'-méthylènebis(phénylisocyanate), de butane-1,4-diol et de poly(éther tétraméthylènique de glycol), en solution et à l'état solide. Les spectres confirment que ces six TPE ont été synthétisés à partir du même mélange de départ constitué de diisocyanate/diol/poly(éther de glycol). Les variations des proportions relatives des diverses matières de départ étaient reflétées par l'intensité des pics de résonance du carbone associés aux parties du polymère riches en uréthane (riche en diisocyanate) et à celles riches en poly(éther de glycol). On a trouvé que les variations du rapport des intensités des pics correspondaient à celles de la dureté Shore D des polymères. On a réalisé une expérience de type Goldman-Shen sur trois de ces TPE. Les résultats obtenus amènent à penser que l'échantillon d'Elastollan 1164D avait un espacement interdomaine plus grand et donc un plus haut degré de séparation des phases que ceux des échantillons de Texin 970D et de Texin 950D.

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Executive summary

Introduction

Poly(ether)urethanes are segmented block copolymers that consist of urethane rich hard segments and poly(ether glycol) rich soft segments. The alternating hard (A) and soft (B) segments result in a block copolymer with the structure $(AB)_n$. The hard and soft segments of poly(ether)urethane elastomers are chemically incompatible. This results in separation of the hard and soft phases of the polymer. The degree of phase separation depends on a number of parameters including the relative proportion of hard and soft segments in the polymer, the method used to synthesize the polymer, and the molecular weight of the poly(ether glycol).

Poly(ether)urethane thermoplastic elastomers (TPEs) have properties that make them ideal candidates for a number of defence applications. By varying the nature and ratio of the material used in their preparation (diisocyanate/poly(ether glycol/diol), TPEs with a broad range of properties can be prepared. Characterization of these materials is of great importance because of the direct relationship between their structure and properties. In this paper, ^{13}C nuclear magnetic resonance (NMR) is used to characterize six commercial poly(ether)urethane TPEs.

Principal Results

The solution and solid state ^{13}C NMR spectra of six poly(ether)urethanes are presented and discussed with respect to their chemical composition. Chemical shift data for the unique carbons in these samples indicated that all were 4-4'-methylenebis-(phenylisocyanate)/poly(tetramethylene ether glycol/1,4-butanediol based TPEs. The intensities of carbons in similar chemical environments in the hard and soft segments of these polymers are related to the percentages of hard and soft segments in the polymers. The ratio of the intensities of these carbons correlated well with the hardness of the samples. The results of the Goldman-Shen experiment suggest that the Elastollan 1164D sample had a larger hard segment domain size than either the Texin 950D or the Texin 970D samples. This is most likely due to different synthesis methods used to prepare the Elastollan 1164D and Texin 950D and Texin 970D samples.

Significance of Results

The ^{13}C NMR results compliment those acquired using infrared spectrometry, pyrolysis gas chromatography, dynamic mechanical analysis and differential scanning calorimetry. The results of the Goldman-Shen experiment suggest that ^{13}C NMR may provide a method of assessing differences in TPEs resulting from phase separation and hard segment domain size.

John A. Hiltz and Michael Lumsden. 2001. ^{13}C NMR Spectroscopy of 4,4'-Methylenebis-(phenylisocyanate)/1,4-Butanediol/Poly(tetramethylene ether glycol) Poly(ether)urethanes. DREA TM 2001-101. Defence Research Establishment Atlantic.

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Introduction
Les poly(éther)uréthanes sont des copolymères séquencés segmentés, constitués de segments durs riches en uréthane et de segments mous riches en poly(éther de glycol). L'alternance des segments durs (A) et mous (B) donne un copolymère séquencé de structure $(AB)_n$. Les segments durs et mous des élastomères de poly(éther)uréthane sont chimiquement incompatibles, ce qui conduit à une séparation des phases dure et molle du polymère. Le degré de séparation de ces phases dépend d'un certain nombre de paramètres, parmi lesquels la proportion relative de segments durs et mous présents dans le polymère, la méthode utilisée pour synthétiser le polymère et le poids moléculaire du poly(éther de glycol) de départ.
Les élastomères thermoplastiques de poly(éther)uréthane (TPE) possèdent des propriétés qui en font des candidats idéaux pour un certain nombre d'applications dans le domaine de la défense. En faisant varier la nature et la composition des mélanges (diisocyanate/poly(éther de glycol)/diol) de départ, on peut préparer des TPE présentant des propriétés très diverses. Étant donné la relation directe existant entre la structure et les propriétés de ces matériaux, leur caractérisation est très importante. Dans cet article, on décrit la caractérisation de six TPE commerciaux à base de poly(éther)uréthane par résonance magnétique nucléaire (RMN) du ^{13}C.
Principaux résultats
On présente les spectres RMN ^{13}C de six poly(éther)uréthanes en solution et à l'état solide et on les interprète en fonction de la composition chimique des composés. Les données sur le déplacement chimique relatif aux atomes de carbone particuliers de ces échantillons indiquent que ce sont tous des TPE à base de 4,4'-méthylènebis(phénylisocyanate), de poly(éther tétraméthylènique de glycol) et de butane-1,4-diol. Les intensités des pics des atomes de carbone dans des environnements chimiques similaires dans les segments durs et mous de ces polymères correspondent aux pourcentages de segments durs et mous présents dans ces polymères. Le rapport entre les intensités des pics dus à ces atomes de carbone correspond de manière étroite à la dureté de ces échantillons. Les résultats obtenus avec l'expérience de type Goldman-Shen amènent à penser que l'échantillon d'Elastollan 1164D comporte un domaine de segments durs de plus grande taille que ceux des échantillons de Texin 950D ou de Texin 970D. Ceci est très probablement dû aux différentes méthodes de synthèse employées pour préparer ces différents échantillons.
Importance des résultats
Les résultats obtenus par RMN ^{13}C viennent compléter ceux obtenus par spectrométrie infrarouge, chromatographie à pyrolyse, analyse mécanique dynamique et calorimétrie différentielle à balayage. Les résultats de l'expérience de type Goldman-Shen amènent à penser que la RMN ^{13}C pourrait fournir une méthode d'évaluation des différences entre les TPE, provenant de la séparation des phases et de la taille du domaine de segments durs.

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Introduction

Poly(ether)urethanes are segmented block copolymers that consist of urethane rich hard segments and poly(ether glycol) rich soft segments. The alternating hard (A) and soft (B) segments result in a block copolymer with the structure $(AB)_n$. The hard and soft segments of poly(ether)urethane elastomers are chemically incompatible. This results in separation of the hard and soft phases of the polymer [1]. The degree of phase separation depends on a number of parameters including the relative proportion of hard and soft segments in the polymer, the method used to synthesize the polymer [2], and the molecular weight of the poly(ether glycol) [3].

Miller et. al. [2] observed that poly(ether)urethanes containing the same amounts of diisocyanate, poly(ether glycol) and chain extender, but synthesized in a single or multi-step process, exhibited different levels of phase mixing. The multi-step synthesis of 4,4'-methylenebis-(phenylisocyanate) (MDI)/poly(ether glycol)/butanediol thermoplastic elastomers (TPEs) resulted in a greater percentage of hard segments containing a single MDI unit than the single step synthesis. The increased solubility of the shorter hard segments in the soft phase resulted in increased mixing of hard and soft segments. This in turn led to an increase in the glass transition temperature of the soft phase. Li et. al. [3] observed for a series of MDI/poly(ether glycol)/diol polymers that the glass transition temperature of the TPEs decreased with increasing polyether glycol molecular weight.

In an earlier paper, the results of the characterization of six commercial poly(ether)urethanes using infrared analysis, pyrolysis gas chromatography/mass spectrometry, dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC) were reported [4]. Analysis indicated that the elastomers were all MDI/poly(tetramethylene ether glycol)/1,4-butanedol based TPEs. In addition, the analysis indicated that TPEs with similar chemical compositions, that is, similar ratios

of diisocyanate, poly(ether glycol), and diol, exhibited different DMA and DSC responses. These were attributed to differences in the degree of phase mixing/separation in the individual TPEs.

In this paper the characterization of the six poly(ether)urethane TPEs using solution and solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy is reported. A major objective of this study was to determine if ^{13}C NMR spectroscopy could provide insight into the differences in the chemistry and structure of these TPEs. Goldman-Shen experiments [5], which have been used to study phase separation [6] and morphology [7] in segmented copolymers, were carried out on three of the TPEs in an attempt to elucidate differences in their structures.

Experimental

Materials

Texin 990A, Texin 950D, and Texin 970D, were supplied by Bayer Polymers, Etobicoke, Ontario, Elastollan 1195A and Elastollan 1164D were supplied by BASF Corporation-Polymers, Wyandotte, Michigan, and Estane 58300 was supplied by B. F. Goodrich, Cleveland, Ohio. The Shore Type A or Shore Type D Durometer hardness of the six thermoplastic elastomers is shown in Table 1.

Table 1. ***Manufacturer, trade name, and Shore Durometer hardness of the thermoplastic poly(ether)urethane elastomers.***

MANUFACTURER	TRADE NAME	SHORE HARDNESS
Bayer Polymers	Texin 990A	90A
Bayer Polymers	Texin 950D	50D
Bayer Polymers	Texin 970D	70D
BASF Plastics	Elastollan 1195A	95A
BASF Plastics	Elastollan 1164D	64D
B. F. Goodrich	Estane 58300	80A

Solution ^{13}C NMR Spectroscopy

Solution ^{13}C NMR spectra were acquired on a Bruker AC-250 (250 MHz H-1/62.9 MHz for ^{13}C) NMR spectrometer. The TPEs, with the exception of Estane 58300, were run in deuterated dimethylacetamide. Estane 58300 was run in deuterated dimethylformamide. A 5 mm probe was used for all solution NMR spectroscopy. Typically 1000 scans were acquired using composite pulse decoupling. The pulse width was 5 μs, the relaxation delay 1s, and the acquisition time was 1.05 s (16K real points over a sweep width of 15.625 kHz).

Solid State ^{13}C NMR Spectroscopy

Solid state ^{13}C NMR spectra were acquired on a Bruker AMX-400 (100.6 MHz for ^{13}C) NMR spectrometer. TPEs samples were powdered and run in a Bruker 4 mm MAS (magic-angle spinning) triple-resonance probe. The pulse sequence involved cross-polarization (CP) with high-power decoupling. For the cross-polarization, the proton 90 degree pulse was typically 4.5 μs with a contact time of 5 ms. The acquisition time was 25.4 ms, the relaxation delay was 5.0 s, and the sweep width was 80645 Hz. Samples were spun at 10 kHz.

The Goldman-Shen experiments were carried out on a Bruker AMX-400 NMR Spectrometer (100.6 MHz for ^{13}C). The samples were prepared in the same manner as the solid state samples and run in a Bruker 4 mm MAS triple-resonance probe. The pulse sequence is shown in Figure 1. Samples were spun at 10 kHz. The acquisition time was 25.4 ms. 1300 scans were acquired using a sweep width of 800 ppm (80645 Hz) and a relaxation delay of 4 sec. A dephasing delay of 70 μs was followed by 12 cross-relaxation delays (spin diffusion times of 0.01 ms, 0.05 ms, 1.00 ms, 2.00 ms, 4.00 ms, 8.00 ms, 12.00 ms, 16.00 ms, 20.00 ms, 30.00 ms, 50.00 ms, and 90.00 ms).

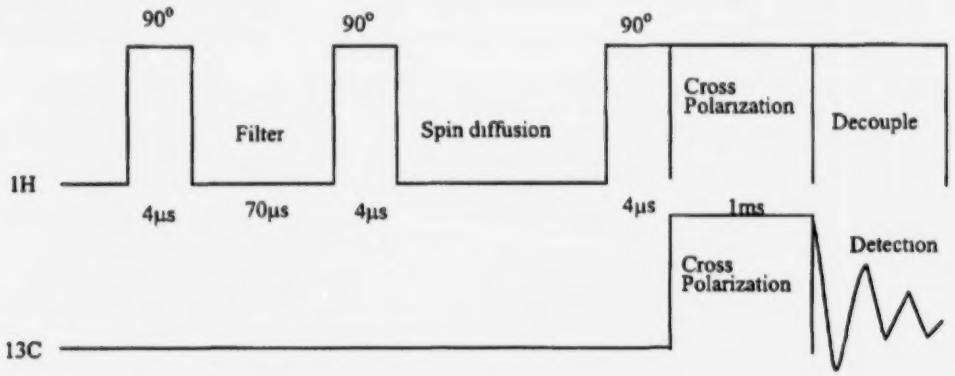

Figure 1. Goldman-Shen pulse sequence. The dephasing delay of 70 ms was followed by 12 cross-relaxation delays.

Results and Discussion

Solution ^{13}C NMR Spectra

The proton decoupled solution ^{13}C NMR spectra of the six TPEs are shown in Figures 2 through 7. The structures of the hard and soft segments of the MDI/poly(tetramethylene ether glycol)/butanediol based poly(ether)urethanes are shown in Figure 8. The chemical shifts of the ten unique carbons in these poly(ether)urethanes, designated C-1 through C-10 in Figure 8, are listed in Table 2. Chemical shifts of the carbons were assigned on the basis of calculated chemical shift data and published chemical shifts for carbons in similar environments.

The resonances centered at 21.7 ppm, 34.7 ppm, 37.5 ppm and the resonance at 171.0 ppm in Figures 2 through 6 arise from the solvent, deuterated dimethylacetamide. As was noted in the Experimental Section, Estane 58300 was run in deuterated dimethylformamide. The resonances centered at 30.6 ppm , 35.7 ppm and 163.2 ppm in Figure 7 are due to deuterated dimethylformamide.

Table 2. Carbon chemical shifts for the six poly(ether)urethanes. Carbons are assigned as indicated in Figure 7.

SAMPLE/ CARBON #	1	2	3	4	5	6	7	8	9	10
Texin 990A	41.76 ppm	137.10	130.45	119.82	139.45	155.43	65.32	27.19	71.77	28.11
Texin 950D	41.73	137.10	130.45	119.82	139.43	155.43	65.32	27.18	71.76	28.11
Texin 970D	41 73	137.15	130.44	119.83	139.42	155.42	65.30	27.18	71.76	28.09
Elastollan 1195A	41.76	137.10	130.45	119.82	139.45	155.43	65.32	27.20	71.77	28.11
Elastollan 1164D	41.73	137.16	130.45	119.82	139.44	155.43	65.31	27.17	71.75	28.09
Estane 58300	ND	136.87	130.07	119.58	138.86	155.07	63.03	26.70	71 30	27.63

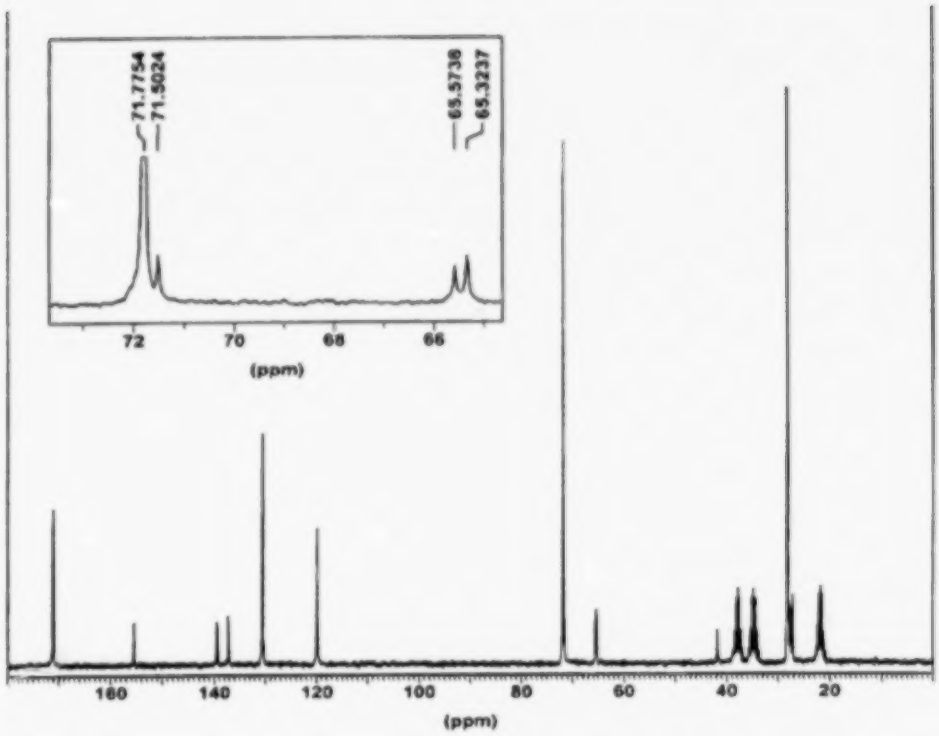

Figure 2. Proton decoupled solution ^{13}C NMR spectrum of Texin 990A thermoplastic elastomer. The solvent was deuterated dimethylacetamide.

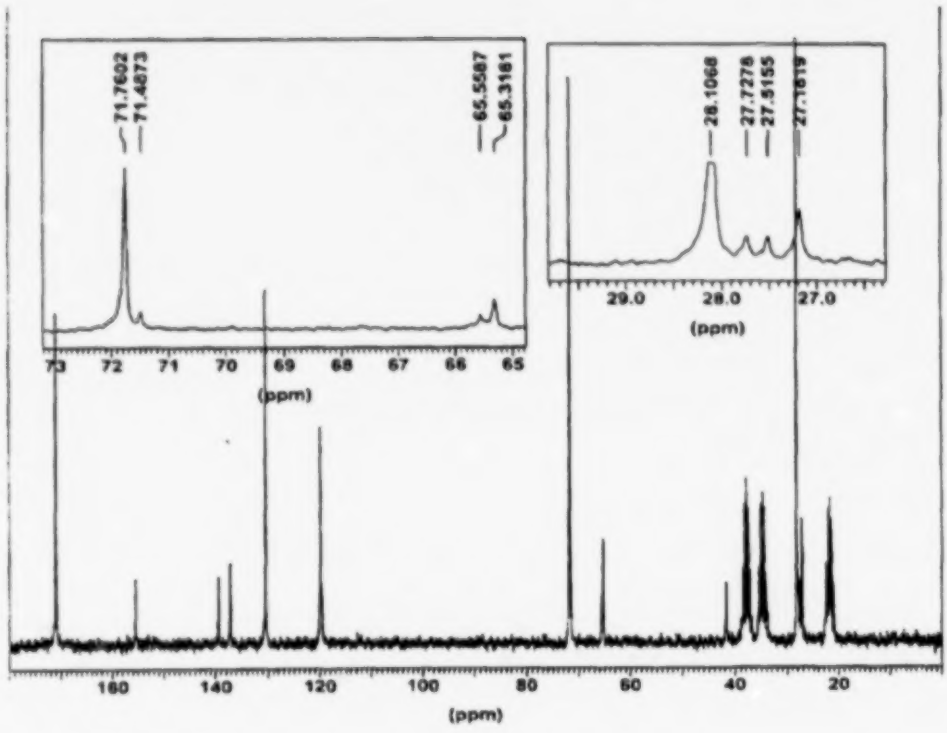

Figure 3. Proton decoupled solution ^{13}C NMR spectrum of Texin 950 D thermoplastic elastomer. The solvent was deuterated dimethylacetamide.

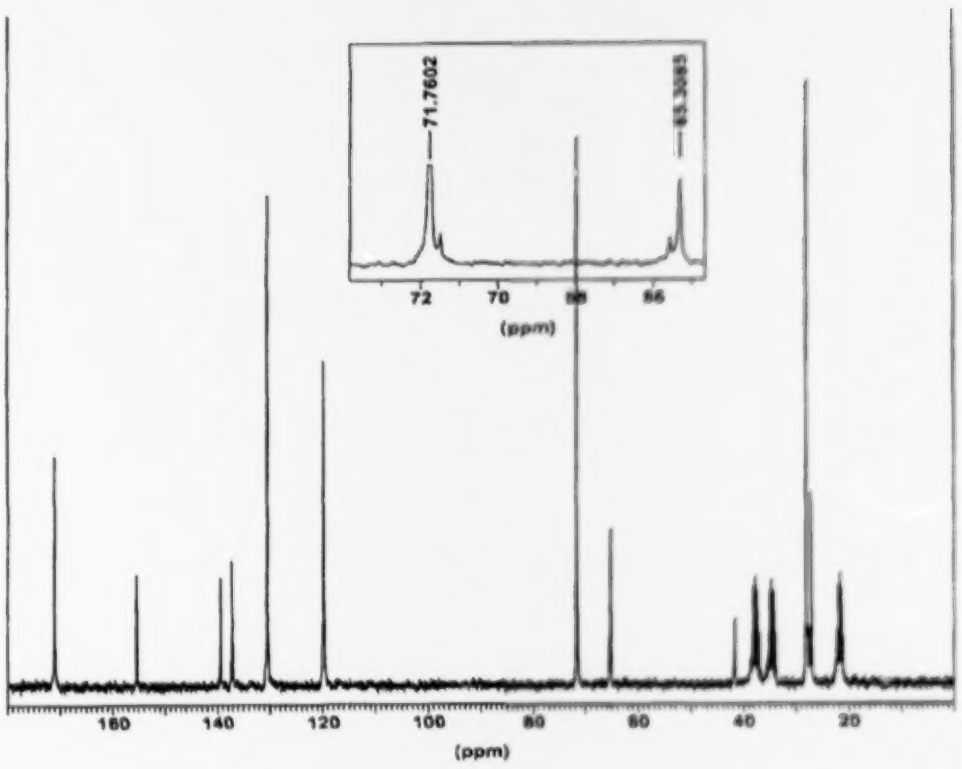

Figure 4. Proton decoupled solution ^{13}C NMR spectrum of Texin 970D thermoplastic elastomer. The solvent was deuterated dimethylacetamide.

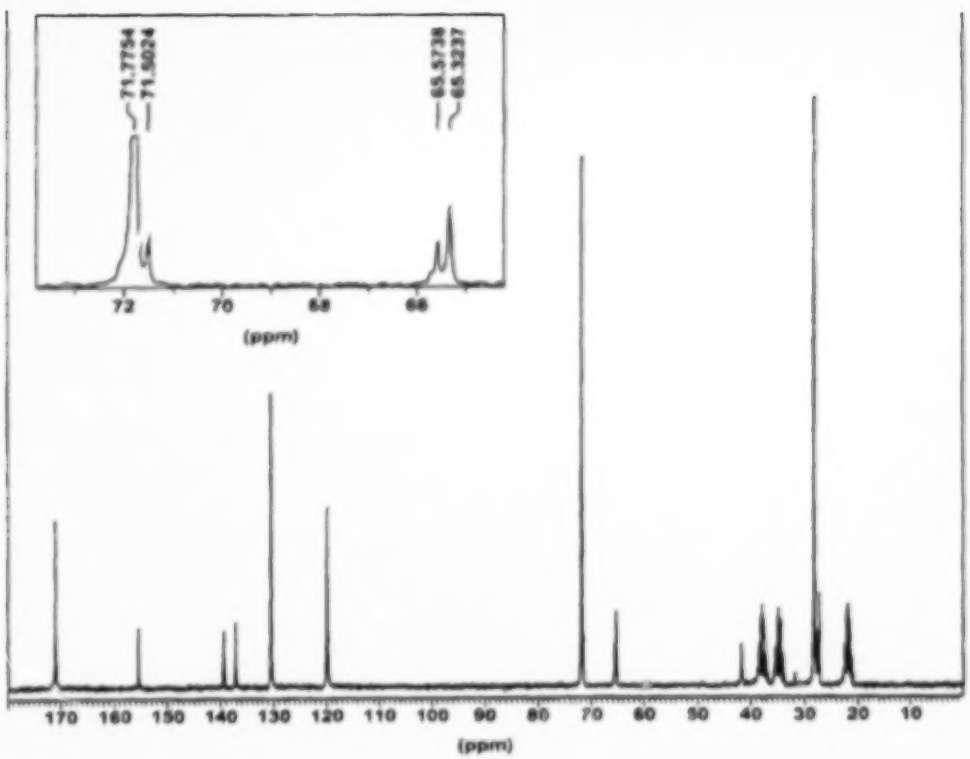

Figure 5. Proton decoupled solution ^{13}C NMR spectrum of Elastollan 1195A thermoplastic elastomer. The solvent was deuterated dimethylacetamide..

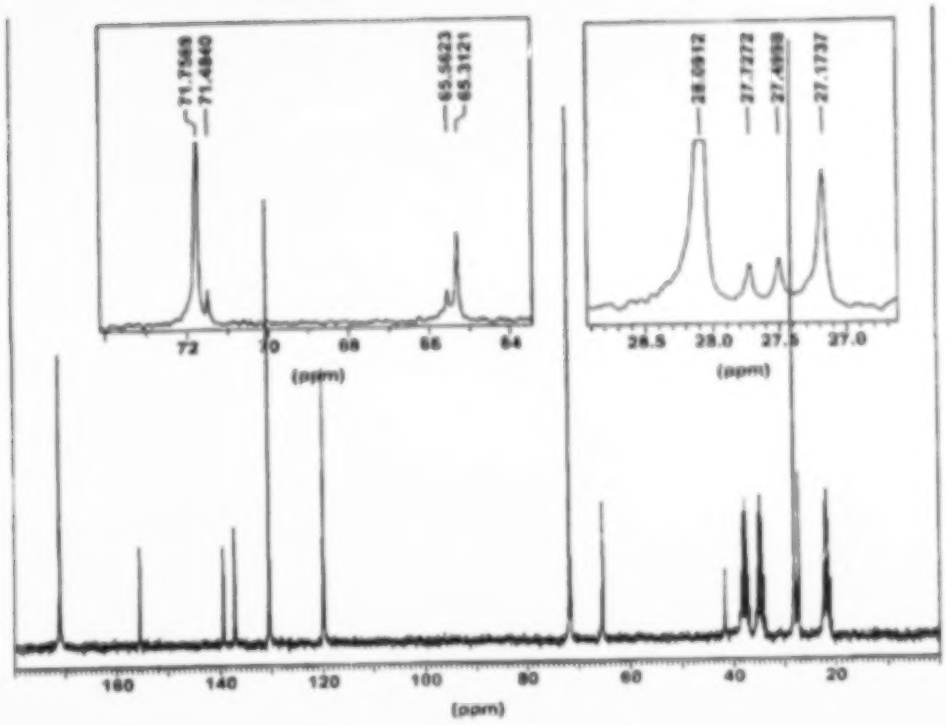

Figure 6. Proton decoupled solution ^{13}C NMR spectrum of Elastollan 1164D thermoplastic elastomer. The solvent was deuterated dimethylacetamide.

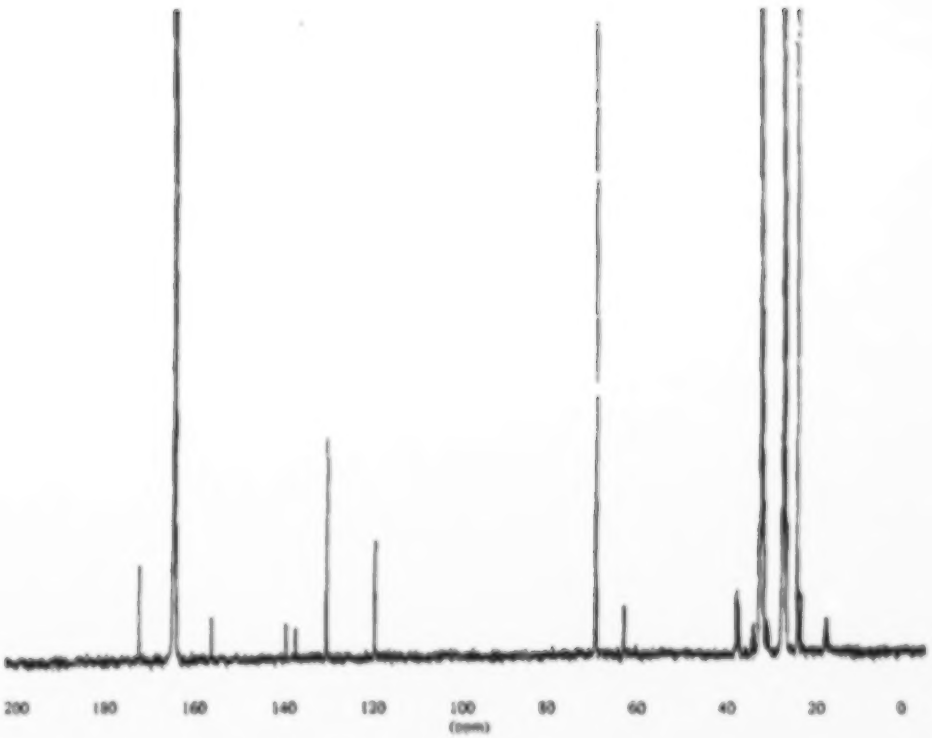

Figure 7. Proton decoupled solution ^{13}C NMR spectrum of Estane 58300 thermoplastic elastomer. The solvent was deuterated dimethylformamide.

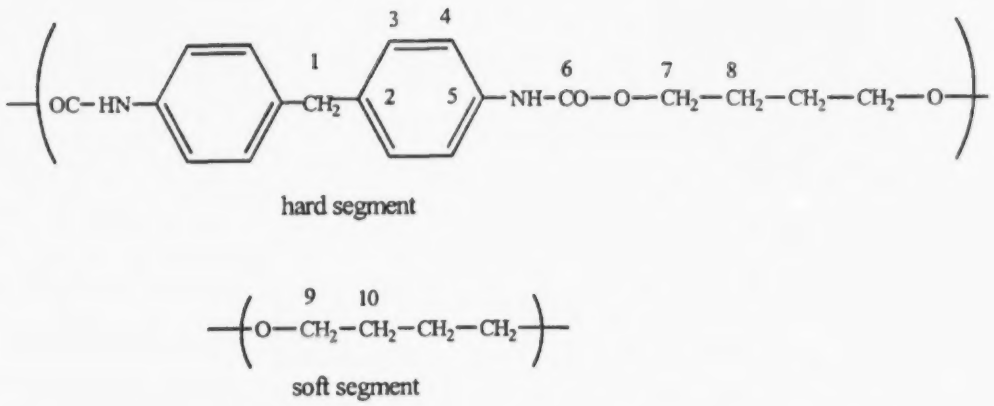

Figure 8. – Structures of the hard and soft segments of the MDI/butanediol/poly(tetramethylene ether glycol) poly(ether)urethanes. The numbers refer to carbons in unique chemical environments.

The chemical shifts of each of the distinct (equivalent) carbons were similar for the six TPEs. For instance, the chemical shift of carbon C-1, the methylene carbon in the hard segment portion of the polymer, varied between 41.73 ppm and 41.76 ppm for the Texin and Elastollan samples. The chemical shifts of the Estane 58300 carbons were slightly less than those for the Texin and Elastollan samples. For instance, the chemical shift of carbon C-2 for Estane 58300 was 136.87 ppm while the chemical shift for carbon C-2 of the other elastomers varied between 137.10 and 137.16 ppm. As the Estane 58300 sample was run in deuterated dimethylformamide rather than deuterated dimethylacetamide, the observed decrease may be due to solvent effects.

The chemical shifts of the carbons for the six TPEs confirm the results of infrared and pyrolysis gas chromatography/mass spectrometry analysis of these elastomers. That is, the starting materials used in their preparation were the same. Although the chemical shifts for equivalent carbons vary little from elastomer to another, a significant variation in the intensities of the carbon resonances was observed.

The intensity of a carbon resonance is related to its abundance in the sample. The intensities of the resonances arising from the O-C*H_2 carbons in the hard (C-7) and soft (C-9) segments and the O-CH_2C*H_2 carbons in the hard (C-8) and soft (C-10) segments are related to the percentages of hard and soft segments in the sample. The relative intensities of carbons C-7, C-8, C-9, and C-10, the ratios of the intensity of carbon C-7 to carbon C-9 and carbon C-8 to carbon C-10, and the Shore D hardness of the six TPEs are listed in Table 3. Comparison of the ratios of the intensities of carbons C-7 to C-9 and carbons C-8 to C-10 for the Texin and Elastollan samples indicates that the number of carbons in the hard segment of the polymer increases as the hardness of the sample increases.

Plots of the ratio of the intensity of carbons C-7 to C-9 and C-8 to C-10 against Shore D hardness are shown in Figures 9 and 10 respectively. The C7/C9 and C8/C10 ratios were found to increase linearly with an increase with Shore D hardness.

*Table 3. **Relative intensities of carbons C-7, C-8, C-9 and C-10, ratios of intensities of C7/C9 and C8/C10 and Shore D hardnesses of the poly(ether)urethanes.***

SAMPLE/INTENSITY	C7	C9	C7/C9	C8	C10	C8/C10	SHORE D HARDNESS
Texin 990A	1.2	11.2	0.11	1.4	12.4	0. 11	39
Texin 950D	2.2	12.1	0.18	2.7	12.9	0.21	50
Texin 970D	3.2	11.4	0.28	4.0	12.7	0.32	70
Elastollan 1195A	1.5	11.0	0.14	1.9	12.3	0.16	46
Elastollan 1164D	2.9	11.4	0.26	3.5	12.8	0.27	64
Estane 58300	1.0	13.3	0.08	1.1	12.8	0.09	29

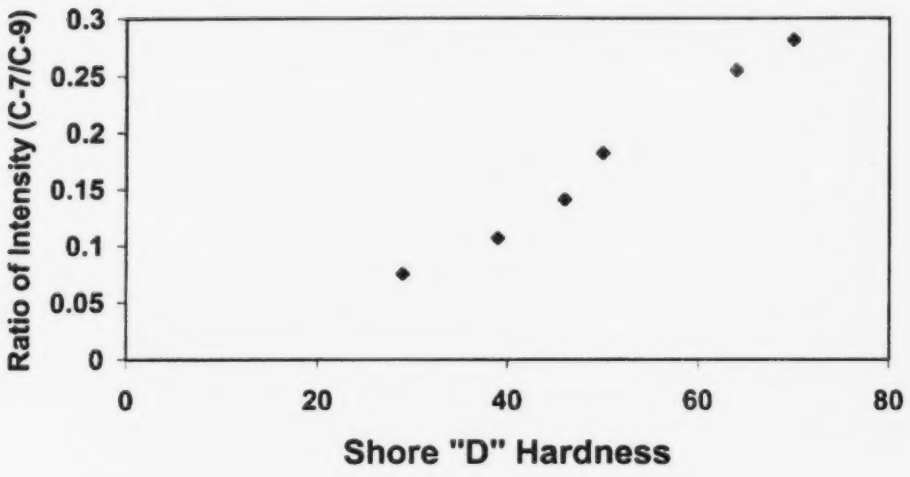

Figure 9. – Plot of the ratio of intensity of carbons C-7 and C-9 against Shore Type D Durometer hardness for the six TPEs.

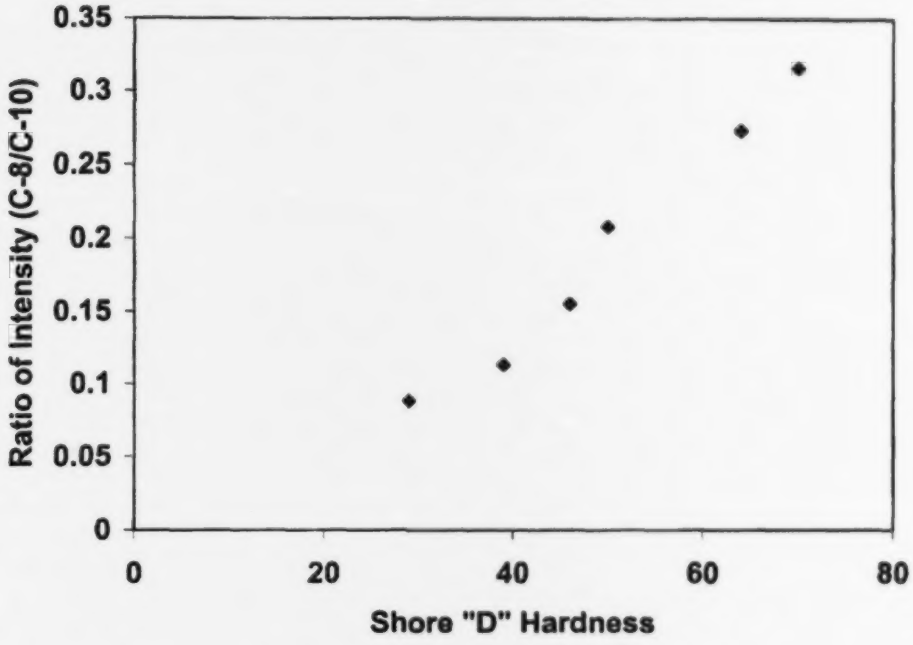

Figure 10. – Plot of the ratio of intensity of carbons C-8 and C-10 against Shore Type D Durometer hardness for the six TPEs.

Solid State ^{13}C NMR Spectra

The ^{13}C NMR solid state spectra of the six TPEs are shown in Figures 11 through 16. The ^{13}C chemical shifts of the six TPEs are listed in Table 4. Eight carbon resonances were observed for the Texin 950D, Texin 970D, Elastollan 1195A and the Elastollan 1164D samples. Comparison of the solid state and solution spectra indicates that the C-8 and C-10 carbons and the C-2 and C-5 carbons are not resolved in the solid state spectra. No resonance was observed for the C-1 carbon of the Texin 990A sample while no resonances were observed for the C-1, C2-, C-3, C-4 and C-5 carbons of the Estane 58300 sample. These resonances arise from the urethane rich portion (hard

segments) of the TPEs and their low intensity is indicative of the low concentration of the hard segments in Texin 990A and Estane 58300 samples.

Table 4. Solid state ^{13}C NMR chemical shifts for TPE elastomers. Carbon numbers are the same as those shown in Figure 7.

SAMPLE/CARBON #	1	2/5	3	4	6	7	8/10	9
Texin 990A	ND	135.70 ppm	130.42	121.11	154.62	65.99	27.27	71.09
Texin 950D	40.61	136.38	130 38	121.42	154.40	65.77	27 06	70 93
Texin 970D	40.33	137.20	129.93	119.78	154.61	65.88	27 20	71.12
Elastollan 1195A	41 22	136.96	130 28	121.83	154.64	65.99	27.31	71 44
Elastollan 1164D	40.80	137.27	130.32	121.80	154.66	65 94	27.17	71.02
Estane 58300	ND	ND	ND	ND	154.65	65 96	27.16	70 96

ND – Not detected

As was noted for the solution NMR spectra, the intensities of the resonances are proportional to the number of carbons in the sample giving rise to them and can be used to determine the relative percentages of hard and soft segments in the sample. The relative intensities of carbons C-7 and C-9, the ratios of the intensity of carbon C-7 and carbon C-9 and the Shore D hardness of the six TPEs are listed in Table 5.

A plot of the ratio of the intensity of carbons C-7 and C-9 against Shore D hardness is shown in Figures 17. In general, the C7/C9 ratio increased with an increase in Shore D hardness. However, the ratio for Elastollan 1164D was greater than that for Texin 970D. It should be noted that the intensity not the area under the resonance peaks was used for the ratio. The discrepancy for the Texin 970D and Elastollan 1164D samples may result from differences in the peak widths. This in turn would cause differences in the relationship between peak height and peak area.

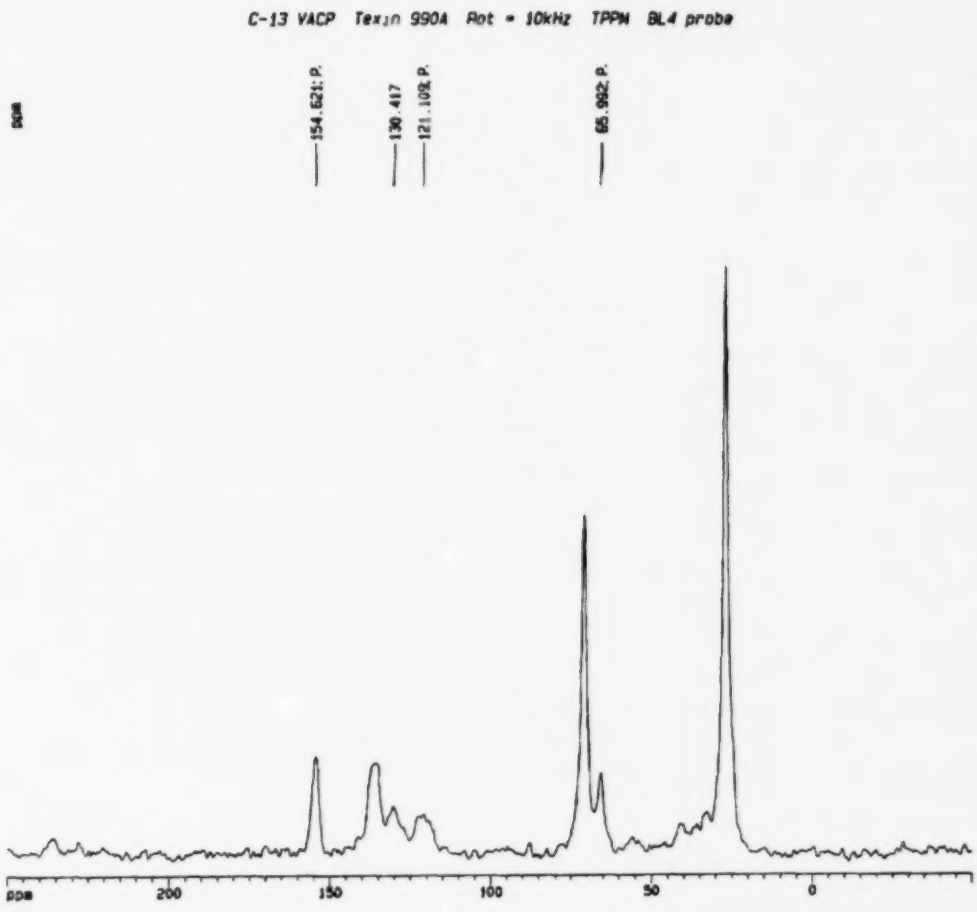

Figure 11. – Solid state ^{13}C NMR spectrum of Texin 990A. The spectrum was acquired using cross polarization with magic angle spinning and high power proton decoupling.

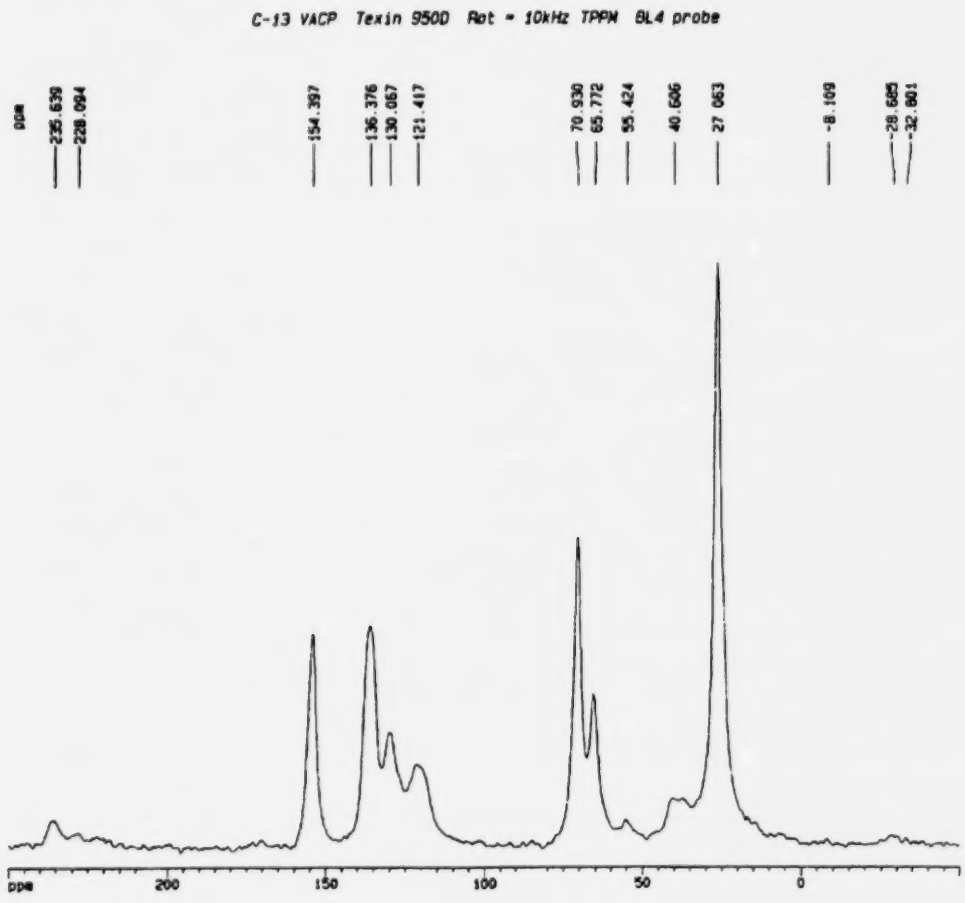

Figure 12. – Solid state ^{13}C NMR spectrum of Texin 950D. The spectrum was acquired using cross polarization with magic angle spinning and high power proton decoupling.

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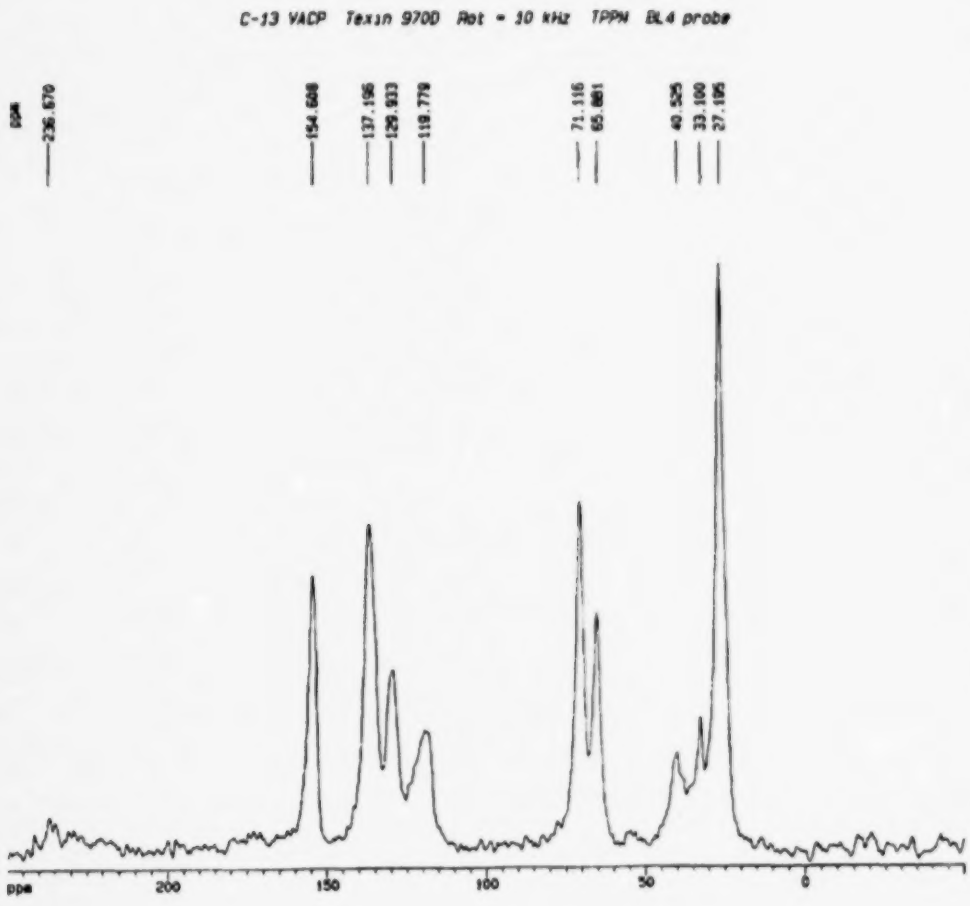

Figure 13. – Solid state ^{13}C NMR spectrum of Texin 970D. The spectrum was acquired using cross polarization with magic angle spinning and high power proton decoupling.

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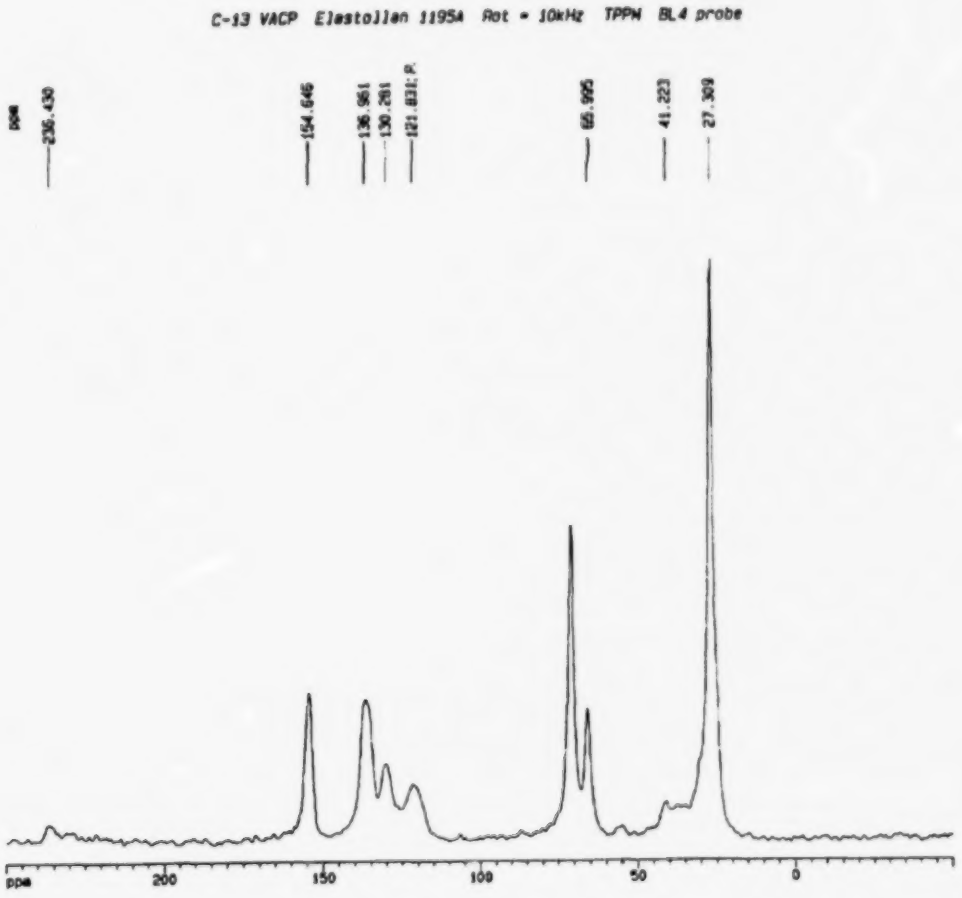

Figure 14. – Solid state ^{13}C NMR spectrum of Elastollan 1195A. The spectrum was acquired using cross polarization with magic angle spinning and high power proton decoupling.

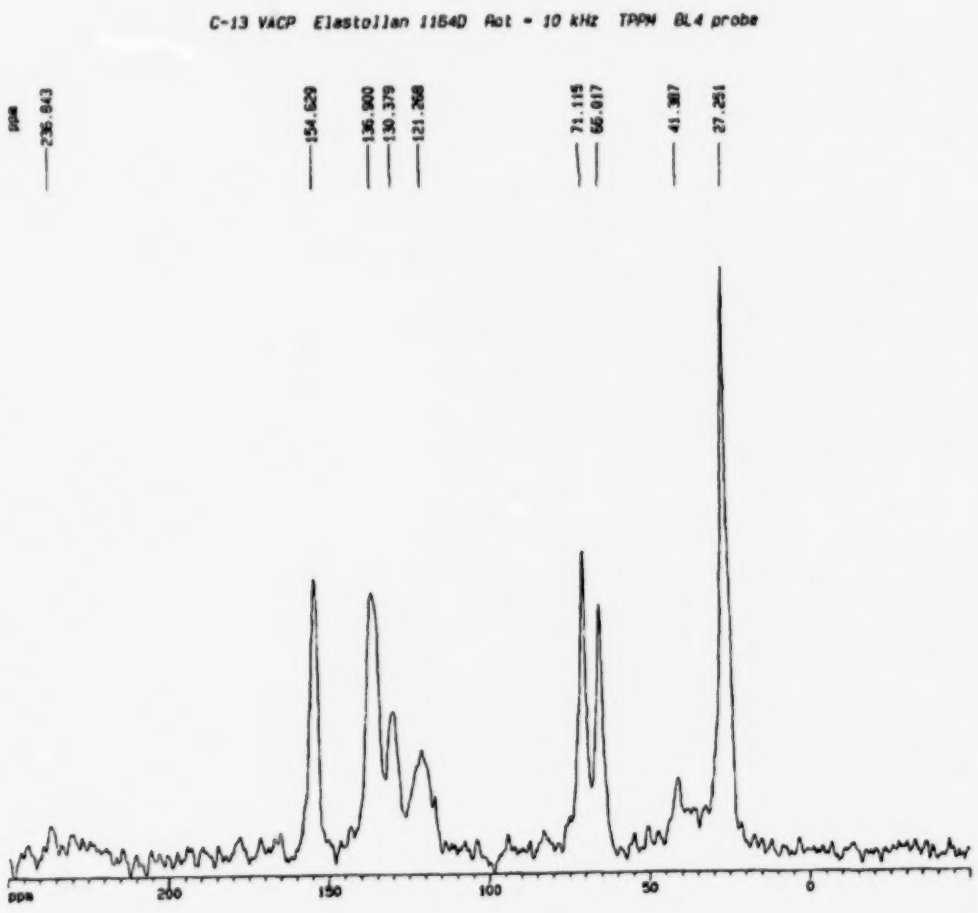

Figure 15. – Solid state ^{13}C NMR spectrum of Elastollan 1164D. The spectrum was acquired using cross polarization with magic angle spinning and high power proton decoupling.

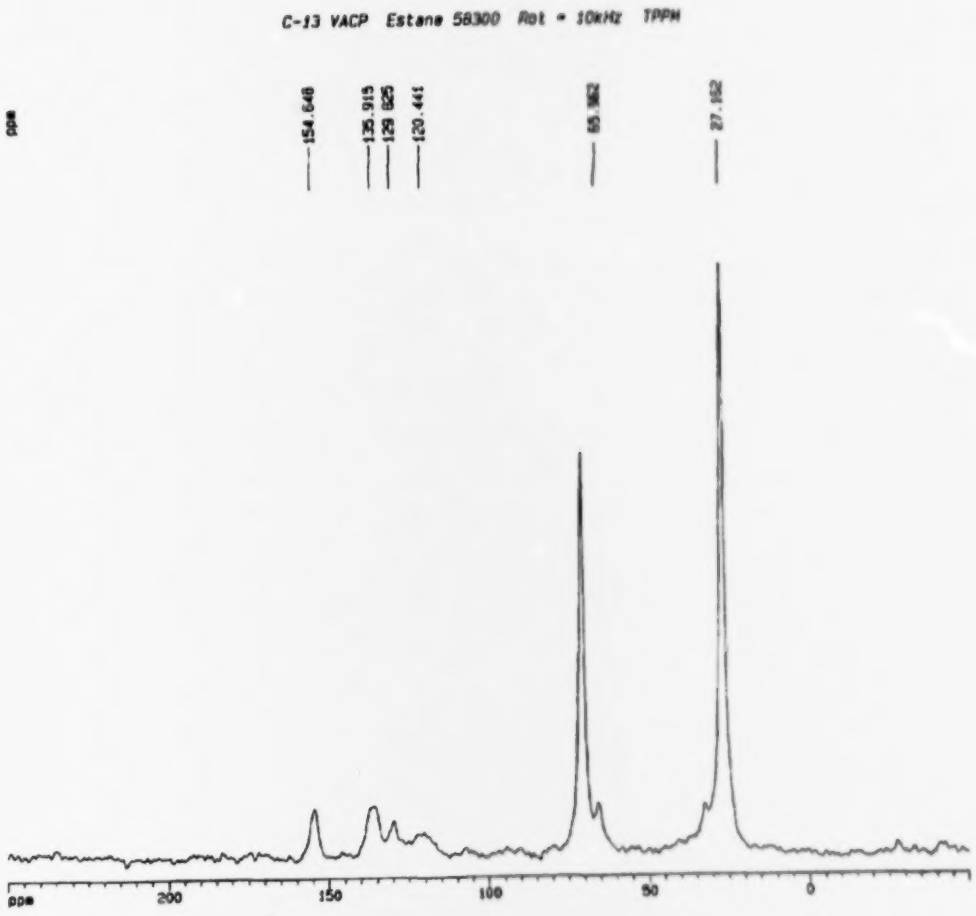

Figure 16. – Solid state ^{13}C NMR spectrum of Estane 58300. The spectrum was acquired using cross polarization with magic angle spinning and high power proton decoupling.

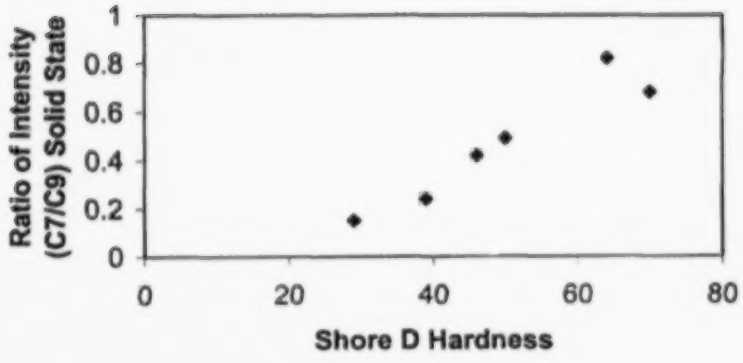

Figure 17. – Plot of the ratio of intensity of carbons C-7 and C-9 against Shore Type D Durometer hardness for the six TPEs.

Table 5. Relative intensities of carbons C-7 and C-9, ratio of intensity of C7 and C9, and Shore D hardnesses of the poly(ether)urethanes.

SAMPLE	C-7 INTENSITY	C-9 INTENSITY	RATIO C-7/C-9	SHORE D HARDNESS
Texin 990A	13.0	54.0	0.24	39
Texin 950D	24.0	49.0	0.49	50
Texin 970D	37.5	55.0	0.68	70
Elastollan 1195A	21.0	50.0	0.42	46
Elastollan 1164D	38.5	47.0	0.82	64
Estane 58300	8.0	53.0	0.15	29

Goldman-Shen Experiment

The Goldman-Shen experiment was carried out to determine if this technique could be used to study differences in the microstructure of chemically similar TPEs.

DMA and DSC analysis had indicated that there were differences in the microstructures, and specifically the degree of phase separation, of the Elastollan 1164D and Texin 950D and Texin 970D samples [4]. For instance, Elastollan 1164D had a glass transition temperature (T_g) of –18.6°C compared to -7.5°C for Texin 950D and 34.8°C Texin 970D. Phase separated TPEs have been observed to have a lower T_g than a more phase mixed TPE with similar chemistry [3]. The Texin samples also had broader loss modulus ($E^{"}$) versus temperature peaks than the Elastollan 1164D sample. Broadening in the peak in a loss modulus versus temperature plot is also indicative of increased phase mixing of the polymer [9].

DSC analysis confirmed that the Elastollan 1164D sample was less phase mixed than the Texin samples. The DSC results also indicated that there were differences in the long range order in the microcrystalline areas of the three polymers. The samples had endothermic peaks in their thermograms that were attributed to the melting of microcrystalline areas. However, the Elastollan 1164D sample had endothermic peaks at higher temperatures that either the Texin 950D or Texin 970D sample. The Elastollan 1164D sample also had a heat of crystallization that was significantly higher than the Texin samples. This is consistent with more long range order in the Elastollan 1164D sample resulting from increased phase separation. What was not obvious from this analysis was why the Elastollan 1164D sample, which infrared and pyrolysis gas chromatography/ mass spectrometry analysis indicated contained less urethane rich hard segment than the Texin 970D sample, was a more phase separated polymer.

It was then postulated that the differences in the DMA and DSC results for the Elastollan 1164D and Texin 950D and Texin 970D might be due to different synthesis methods. .Miller et. al. [2] found that the method used to synthesize poly(ether)urethanes had a significant effect on their degree of phase separation. A one step synthesis produced a larger proportion of hard segments containing more than one MDI unit than a multi-step synthesis. Hard segments containing more MDI units are less soluble in the soft segments and therefore increase the degree of phase separation. Also, one might expect that the larger hard segments would form larger microcrystalline domains The Goldman-Shen experiment was carried out to determine if there were differences in the hard segment domain sizes in the Elastollan and Texin samples.

The experiment probes differences in the spin-spin relaxation properties of nuclei that arise due to differences in the mobility of the hard and soft segments of the polymers. The nuclei in the more rigid hard segments have a shorter T_2 relaxation time than the nuclei in the more mobile soft segments. The experiment demagnetizes the nuclei in the hard segment and monitors the rate of remagnetization of the hard segment nuclei resulting from the magnetization diffusion from the soft segment nuclei. The rate of spin diffusion depends on interdomain spacing and the interdomain spacing is indicative of the degree of phase separation in the sample. A larger domain size is associated with a slower rate of diffusion or a longer diffusion time.

The relationship between the diffusive path length (interdomain spacing), L, and the diffusion time, τ, are given by equation 1, where D is the diffusion coefficient [8].

$$\langle L^2 \rangle \sim 6D\tau \qquad (1)$$

It can be seen from equation 1 that as the diffusion time increases (or the rate of diffusion decreases) the interdomain spacing increases.

The remagnetization of the hard segment O-CH_2 carbon (carbon C-7 in Figure 8) was monitored in the experiment. Plots of the normalized intensity of the O-CH_2 carbon (hard segment) against the square root of spin diffusion time (τ) for Texin 950D, Texin 970D and Elastollan 1164D is shown in Figure 18. Although the data shows some scatter, the diffusion time for the Elastollan 1164D sample is longer than the diffusion times for the Texin samples. This suggests that the interdomain spacing and therefore the hard segment domain size is greater in the Elastollan 1164D sample than in the Texin samples. This provides evidence that the difference in the DMA and DSC results for these TPEs arise from differences in the synthetic method used in their preparation.

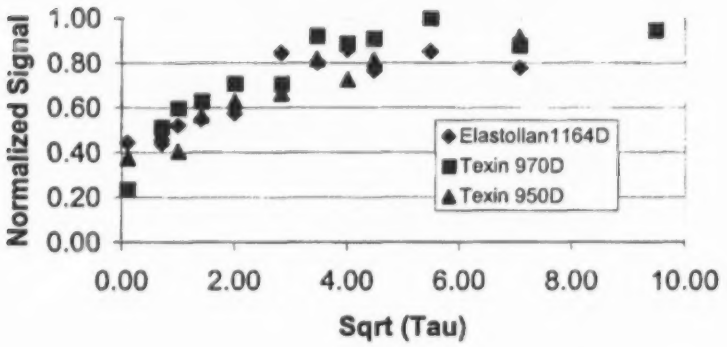

Figure 18. Plot of normalized intensity of O-CH_2 carbon against the square root of spin diffusion time for Texin 950D, Texin 970D and Elastollan 1164D.

Conclusions

The solution and solid state ^{13}C NMR spectra of six poly(ether)urethanes are presented. Chemical shift data for the unique carbons in these samples indicate that all were 4-4'-methylenebis-(phenylisocyanate)/poly(tetramethylene ether glycol/1,4-butanediol based TPEs. The intensities of carbons in similar chemical environments in the hard and soft segments of these polymers are related to the percentages of hard and soft segments in the polymers. The ratio of the intensities of these carbons correlates well with the hardness of the samples. The results of the Goldman-Shen experiment suggest that the Elastollan 1164D sample had a larger hard segment domain size than either the Texin 950D or the Texin 970D samples. This is most likely due to different synthetic methods used to prepare the Elastollan and Texin samples.

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The solution and solid state ^{13}C NMR spectra of six 4,4'-methylenebis-(phenylisocyanate)/1,4-butanediol/poly(tetramethylene ether glycol) based poly(ether)urethane thermoplastic elastomers (TPEs) are presented. The spectra confirm that all six TPEs were synthesized from the same diisocyanate/diol/polyether glycol starting materials. Changes in the relative proportions of the starting materials were reflected in the intensity of carbon resonances associated with the urethane rich (diisocyanate rich) and polyether glycol rich portions of the polymer. Changes in the ratio of the intensities of carbons were found to correlate with the Shore D hardness of the polymers. A Goldman-Shen experiment was conducted on three of the TPEs. The results suggest that the Elastollan 1164D sample had larger interdomain spacing and therefore a greater degree of phase separation than the Texin 970D and Texin 950D samples.

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solution NMR
solid state NMR
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poly(tetramethylene ether glycol)
1,4-butanediol

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